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54 **Process for desensitising 2,4,6-trinitrotoluene, solutions thus obtained and their application for preparing phloroglucinol.**

57 A process for desensitizing the explosive 2,4,6-trinitrotoluene (TNT) by preparing a solution of TNT in oleum of which the strength may vary from 10 to 40% (by weight) as well as solutions thus obtained are described. Preferably, at least 400 g and at most 480 g of TNT are dissolved per litre oleum of 20-25%.

The solutions of TNT in oleum thus obtained are especially useful for the preparation of phloroglucinol.

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DESENSITIZED TNT: PROCESS AND APPLICATION

The present invention relates to a process for desensitizing the explosive 2,4,6-trinitrotoluene, hereinafter abbreviated to TNT. The invention also relates to solutions of TNT in very strong sulfuric acid as well as to their application for the preparation of phloroglucinol.

Desensitizing is understood to mean here the minimization of the sensitivity of an explosive compound to heat and shock without it costing the compound's explosive force. The purpose of desensitization is a safer handling of the explosive compound.

Desensitization of explosive compounds, especially of high-explosives, is already known. Urbanski and Galas, for example, mention in C.r. 209 (1939) 558 the addition of non-explosive liquids, such as chloroform, n-heptane, acetone, H_2O and glycerin, while the French Patent Specification 863 154 describes how the shock sensitivity of explosive compounds, including TNT, can be diminished by mixing or enveloping the explosive compound with a waxy or fatty material, such as paraffin wax or a stearate.

The French Patent Specifications 2 102 642 and 2 102 815 describe a process of desensitization in which the granular explosive compound is enveloped with a layer of natural or synthetic wax of which the melting point ranges preferably between 60° and 72°C.

Also the German Patent Application 2 308 430, laid open for public inspection, relates to a way of desens-

itizing, in which the granular high-explosive substance is coated with a layer of wax, but then the grains thus coated are dried and subsequently tempered.

The German Patent Application 2 349 640, laid open
5 for public inspection, cites mono-, di- and trinitro-derivatives of benzene, toluene, xylene, etc. as examples of desensitizing agents for gelatinous explosive compounds. In other words: here, TNT itself is proposed as a desensitizing agent.

10 All the methods of desensitization mentioned above have the disadvantage that the desensitizing effect is insufficient, as will be further demonstrated below. Moreover, in those desensitizing methods only the application of the desensitized compound as an explosive
15 has been considered. In that case the presence of or envelopment with a comparatively small amount of an inert substance is not inconvenient. In the present case, however, where the TNT is used as a starting material for the preparation of phloroglucinol, the presence of
20 inert substances or the envelopment with layers of wax is highly inconvenient, because these must be removed before, the desensitizing effect thus being lost at the same time.

The object of the present invention is to provide a desensitizing process that does not present the draw-
25 backs mentioned above.

Consequently, the invention relates to a process for desensitizing the explosive TNT, in which there is prepared a solution of TNT in oleum of which the strength (= amount of SO_3 dissolved therein) may vary from 10 to
30 40% (by weight).

Though every gramme of TNT dissolved in oleum is desensitized, desensitizing is only of some practical importance, of course, if at least a certain amount of TNT has been dissolved. Here, an amount of 80 g per
35 litre oleum 10% is chosen as a practical lower limit.

The upper limit is determined by the desired degree of desensitization, for the more TNT is dissolved, the more

quickly the TNT will crystallize out of the solution - and crystallized TNT is no longer in a desensitized state. As an upper limit an amount of 600 g of TNT per litre oleum 40% is chosen.

- 5 It is advantageous to start from the commercially available oleum in which 20 to 25% by weight of SO_3 (in short: oleum 20-25%) has been dissolved and preferably the amount of TNT to be dissolved in it ranges from 320 to 500, more particularly from 400 to 480 g per
10 litre oleum.

When a solution of 480 g of TNT per litre oleum 20-25% is stored for 5 x 24 hours at 0°C , the TNT will not crystallize out, even not if the solution is injected with crystalline TNT.

- 15 In a solution of 400 g of TNT per litre oleum 20-25%, crystallization will not even occur at -10°C after the solution is allowed to stand for 5 x 24 hours, nor does it when TNT seed crystals are added to this solution.

The desensitizing effect of oleum, as well as that of
20 other desensitizing means, on the explosiveness of TNT when subjected to shock, friction and heat, is evident from the measuring results shown in the table. The values for the sensitivity to shock, friction and heat have been determined according to the statutory methods applied in
25 defining the dangerous materials classes for the transportation of dangerous substances. The said methods are assumed to be known to those skilled in the art. The table also includes the requirements desensitized TNT must meet in order to have been desensitized such as
30 to fall beyond the class to which the transport regulations for substances involving explosion hazard are applicable.

Table

		Sensitivity to shock (in kgm)	Sensitivity to friction (in kgf)	Sensitivity to heat (in mm)
5	TNT pure	2.4	> 36	5 to 8
	Requirements in transport regulations for dangerous substances	> 5	> 36	< 1
10	TNT/talc powder			
	wt/wt 80/20	2.5	> 36	4 to 6
	70/30	3	> 36	2
	TNT/paraffin wax			
	wt/wt 80/20	3.9	> 36	3
15	70/30	6.3	> 36	1.5
	60/40	7.3	> 36	2
	40/60	-	> 36	> 1
	TNT/Nibren* wax			
20	wt/wt 80/20	9.4	> 36	3
	TNT/kieselguhr			
	wt/wt 80/20	-	-	2
	60/40	0.5	-	0
25	TNT/oleum 20% 600 g / L	> 120	> 36	< 1

* Nibren = mixture of tetrachloronaphthalene

30 From the table it follows that in respect of its
sensitivity to heat, TNT is properly desensitized with
kieselguhr but, on the other hand, becomes more sens-
itive to shock, whereas with paraffin wax it is possible,
indeed, to satisfy the requirements in respect of the
35 sensitivity to shock but not so in respect of the sens-

itivity to heat. None of the said desensitizing means talc powder, paraffin wax, Nibren wax or kieselguhr is capable of desensitizing TNT in a sufficient degree.

The table shows the superb desensitizing effect of
5 oleum: with one litre of oleum 20% it is possible to desensitize 600 g of TNT so that it loses its nature of being a dangerous explosive compound.

Although TNT can also be desensitized by dissolving it in concentrated sulphuric acid (i.e. being at most
10 100%), this has no practical value because of the too low solubility of TNT in concentrated sulphuric acid.

Wetting of the TNT with concentrated sulphuric acid has an insufficient desensitizing effect. In testing the sensitivity to heat of, for example, mixtures of
15 1,000 g of TNT with 250 to 1,000 ml of concentrated sulphuric acid there are obtained values exceeding 1 mm.

In view of the fact that, in general, in particular however for dangerous explosive compounds such as TNT, the
20 safety and environmental regulations are becoming more and more stringent, the importance of the desensitizing process found is evident. The desensitization now found has considerable consequences for the storage, transportation, handling and processing of TNT.

25 Thanks to desensitization the TNT can now be stored in areas and buildings, and in ways which, as a rule, are unacceptable for TNT as an explosive compound. For example, as the TNT is present in a dissolved state, it can be stored in tanks and pumped.

30 To the transportation it applies that if the TNT has been desensitized according to the invention, the carriage may be effected by tank car, in which case the transportation is placed in another, lower dangerous materials class, with all its attendant advantages.

35 As solutions of TNT in oleum of 10% and higher are new, the invention in view of its importance as outlined above, is also directed on that kind of solutions.

Consequently, the invention also relates to solutions of TNT in very strong sulphuric acid, in which per litre oleum, whose strength may vary from 10 to 40%, at least 80 and at most 600 g of TNT are dissolved, the amount being
5 dependent on the strength chosen for the oleum. Solutions containing at least 320 g and at most 500 g, more particularly 400 to 480 g of TNT per litre oleum of 20-25%, are preferred.

An additional, very important advantage of the TNT
10 solutions according to the invention lies in that they can be employed as such for the large-scale manufacture of phloroglucinol.

Consequently, the invention is also directed on a process for the preparation of phloroglucinol from TNT, in which
15 process the TNT, dissolved in concentrated sulphuric acid, is converted by oxidation into 2,4,6-trinitrobenzoic acid, which acid is reduced to 2,4,6-triaminobenzoic acid which in turn is hydrolysed and decarboxylated, the process being characterized in
20 that there is started from TNT which is desensitized according to the invention.

The resulting advantages are many, such as:

- eased transport from yard to reaction vessel
- the prior dissolving of TNT in sulphuric acid is no
25 longer necessary
- until the reaction process the TNT is in the desensitized state
- saving of energy and gain of time.

The saving of energy and gain of time realized are due to
30 the fact that the conversion by oxidation into trinitrobenzoic acid occurs in a sulphuric acid medium of lower than 100%, so that the TNT solutions according to the invention must be diluted. The heat released in that process can serve as the necessary heat of reaction for
35 the oxidization step.

In other words: the warming-up step is omitted, energy and time thus being gained.

The following example serves to illustrate the invention.

250 ml of fuming sulphuric acid, containing 20% by weight of SO_3 (oleum 20%) are set stirring while being
5 sealed against moisture. To this solution 100 g of TNT in the form of flakes are added in portions at room temperature. Stirring is continued until all the TNT has been dissolved.

CLAIMS

1. Process for desensitizing the explosive 2,4,6-trinitrotoluene (TNT), characterized in that there is prepared a solution of TNT in oleum of which the strength may vary from 10 to 40% (by weight).
- 5 2. Process according to claim 1, characterized in that at least 80 and at most 600 g of TNT are dissolved per litre oleum, the amount being dependent on the strength chosen for the oleum.
3. Process according to claim 1 or 2, characterized
10 in that at least 320 and at most 500 g of TNT are dissolved per litre oleum of 20-25%.
4. Process according to any one of the claims 1-3, characterized in that at least 400 and at most 480 g of TNT are dissolved per litre oleum of 20-25%.
- 15 5. Solution of 2,4,6-trinitrotoluene (TNT) in very strong sulphuric acid, characterized in that per litre oleum whose strength may vary from 10 to 40%, at least 80 and at most 600 g of TNT have been dissolved, the amount being dependent on the strength of the oleum.
- 20 6. Solution according to claim 5, characterized in that at least 320 and at most 500 g of TNT have been dissolved per litre oleum of 20-25%.
7. Solution according to claim 5 or 6, characterized in that at least 400 and at most 480 g of TNT have been
25 dissolved per litre oleum of 20-25%.
8. Process for preparing phloroglucinol from 2,4,6-

trinitrotoluene (TNT), in which the TNT, dissolved in concentrated sulphuric acid, is converted by oxidation into 2,4,6-trinitrobenzoic acid, which acid is reduced to 2,4,6-triaminobenzoic acid which in turn is hydrolysed and
5 decarboxylated, the process being characterized in that there is started from TNT which is desensitized according to any one of claims 1 to 4.

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European Patent
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EUROPEAN SEARCH REPORT

Application number
EP 80 20 0124

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<p>INDUSTRIAL AND ENGINEERING CHEMISTRY, vol. 42, (1950) M.L. KASTENS et al. "TNT into Phloroglucinol", pages 402-413.</p> <p>* Page 406, right-hand column, line 25 - page 409, left-hand column, line 9; page 411, left-hand column 4th paragraph *</p> <p>--</p>	1-8	C 07 C 79/10 37/045 39/10
DA	<p>DE - A - 2 308 430 (MESSERSCHMITT-BOLKOW-BLOHM GmbH)</p> <p>----</p>	1	<p>TECHNICAL FIELDS SEARCHED (Int. Cl.):</p> <p>C 07 C 79/10</p> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons</p> <p>Δ: member of the same patent family corresponding document</p>
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	07-05-1980	SUTER	

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